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PATENT SPECIFICATION

702,013

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COMPLETE SPECIFICATION

Sulphonate Detergent

We, CALIFORNIA RESEARCH CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, and having Offices at 200, Bush Street, San Francisco 4, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved solid, particulate, detergent compositions containing mixtures of sulfonated derivatives of phenyl-substituted alkanes. More particularly it relates to solid, particulate, alkyl benzene sulfonate detergent compositions having reduced caking tendency, in which one of the effective organic detergent ingredients is a water-soluble salt of a mixture of sulfonated monophenyl - substituted acyclic propylene polymers containing from 9 to 1 carbon atoms in the polymer portion of the molecule.

The greater proportion of detergent compositions which owe their detergency to the presence of water-soluble salts of sulfonated phenyl - substituted alkanes are distributed on the market in solid form, either as beads, flakes, chips, scales or granules, packaged into containers, e.g., metal drums, glass jars, wooden boxes or cartons. Practically of these particulate solid detergent compositions, when stored in containers, and particularly when stored in cartons or wooden boxes, are subject to the drawback of caking which occurs even though the material is tightly covered up or sealed in the containers. The occurrence of caking is believed to be due to a number of factors: It may be due in part to the residual moisture of the dry detergent particles; it may also be due to the atmospheric moisture which slowly penetrates into the container, even though it is well sealed; and, finally, the particular physical structure or chemical nature of the detergent particles may contribute to the phenomenon of caking. This occurrence of caking is highly undesirable, because the ultimate consumer requires a product flowing freely from the package, and forming no lumps difficult to dissolve in water.

We have found that this undesirable caking, which is an inherent drawback of practically all sulfonate detergents, can be made substantially non-existent in the case of detergent compositions containing water-soluble salts composed of inorganic cations and mixtures of sulfonated monophenyl-substituted propylene polymers, in which the polymer portion contains from 9 to 18 carbon atoms.

The term "water-soluble salts composed of inorganic cations and mixtures of sulfonated monophenyl-substituted acyclic propylene polymers" as used in this specification includes not only the readily water-soluble salts of alkali metals such as sodium, potassium and lithium, but also salts of ammonium, and salts of alkaline earth metals such as magnesium or calcium, which, even though they do not form true aqueous solutions, may form stable aqueous dispersions.

These water-soluble salts of sulfonated monophenyl-substituted acyclic polymers of propylene may be prepared by condensing propylene polymers containing from 9 to 18 carbon atoms, and preferably from 12 to 15 carbon atoms, with benzene in the presence of hydrofluoric acid as a catalyst, separating from the alkylation product mixture a fraction of monophenyl-substituted propylene polymers which boils from about 475° F. to about 650° F., and sulfonating this fraction with a suitable sulfonating agent, whereupon the sulfonated hydrocarbons are neutralized to form the desired water-soluble salts composed of an inorganic cation and an anionic sulfonic acid radical attached to the phenyl group

[*Price* 2/8]

of the phenyl substituted propylene polymer as a result of the sulfonation treatment. The neutralized sulfonate product in the form of an aqueous slurry or paste may thereafter be compounded, if so desired, with builders, and other additives, and, finally, dried and reduced to the desired particulate, solid form. Further details of the process for the preparation of sulfonated monophenyl-substituted acyclic propylene polymers and of their water-soluble salts, wherein the cation is inorganic, may be obtained from the description given in British Patent No. 645,129.

We have now found that the caking tendency of detergent compositions containing water-soluble salts composed of an inorganic cation and a mixture of sulfonated monophenyl - substituted acyclic propylene polymers, having from 9 to 18 carbon atoms, and preferably from 12 to 15 carbon atoms, in the polymer portion of their molecule, can be substantially reduced, if not wholly eliminated, by replacing at least 20% by weight of the effective detergent ingredient of said composition, i.e., the water-soluble salt composed of an inorganic cation and a mixture of sulfonated monophenyl-substituted acyclic propylene polymers, by an equivalent amount by weight of a water-soluble salt composed of the same cation and a sulfonated 2-phenyl alkane in which the alkane portion is a normal straight-chain alkane containing from 10 to 16 carbon atoms and preferably from 12 to 14 carbon atoms. This reduction of the caking tendency by the introduction of the aforementioned water-soluble salts of sulfonated 2-phenyl alkanes is noted to occur whenever the 2-phenyl alkane sulfonate salt is added in the amount of at least 20% by weight, based on the total weight of the sulfonates in the detergent composition. Addition of from about 25 to about 60% by weight of 2-phenyl alkane sulfonate is recommended for the preparation of economical and satisfactory, non-caking detergent compositions, although amounts in excess of 60% and as high as 95% by weight would be also operative.

Detergent compositions, which owe their detergency to the presence of water-soluble salts composed of inorganic cations and sulfonated monophenyl-substituted propylene polymers having from 9 to 18 carbon atoms in the polymer portion and which can be rendered resistant to caking by the introduction of 20% or more by weight of a water-soluble salt composed of the same inorganic cation and a sulfonated 2-phenyl alkane in accordance with the invention, may be " built " in conformity with the well-established practices of manufacturing synthetic alkyl aromatic sulfonate detergent compositions, i.e., they may contain conventional amounts from 40% to 85% by weight of inorganic builders (based on the total weight of the solids in the detergent composition). Such builders are represented by water-soluble inorganic sulfates and phosphates, e.g., sodium sulfate, sodium tetrapyrophosphate, and sodium tripolyphosphate, and while the presence of these builders may occasion some variation of the caking tendency of the detergent compositions which contain them, it does not interfere to any large degree with the beneficial anti-caking effect of the water-soluble salts composed of inorganic cations and sulfonated 2-phenyl alkanes.

The procedure for the introduction of water-soluble sulfonates of 2-phenyl alkanes into the detergent composition to be stabilized against caking is relatively simple. A mixture of the water-soluble salt composed of an inorganic cation and sulfonated monophenyl - substituted acyclic propylene polymers with at least 20% by weight of a water-soluble salt composed of the same inorganic cation and a sulfonated 2-phenyl alkane may be made up into an aqueous slurry or solution, and this slurry or solution containing about 50% by weight of water is then subjected to drying and reduction to the desired particle size by any conventional technique, e.g., drum-drying or spray-drying.

A more efficient and preferred procedure for preparing improved non-caking detergent compositions of the invention consists in first blending together a mixture of monophenyl-substituted C_9—C_{15} propylene polymers and a 2-phenyl alkane containing from 10 to 16 carbon atoms, and preferably from 12 to 14 carbon atoms, in the alkane portion, in an amount equal from at least 20% to as high as 95%, and preferably from 25% to about 60% of the combined weight of monophenyl-substituted propylene polymers and 2-phenyl alkane. Thereupon, the blend is sulfonated with an appropriate sulfonating agent, such as fuming sulfuric acid or sulfur trioxide, and the resulting sulfonation reaction product is neutralized, dried, and reduced to the desired particulate form and size.

As pointed out hereinbefore, water-soluble salts of sulfonated 2-phenyl alkanes to be employed for the reduction of caking in accordance with the present invention, contain from 10 to 16 carbon atoms, and preferably from 12 to 14 carbon atoms, in the alkane portion. All of these salts are excellent detergents *per*

se, comparable in their detergent power to the corresponding salts of sulfonated monophenyl-substituted C_9 to C_{18} propylene polymers, and their addition does not impair the detergent characteristics of these salts of sulfonated monophenyl-substituted propylene polymers.

Mixtures of 2-phenyl alkanes containing from 10 to 16 carbon atoms in the alkane portion may also be employed for the reduction of caking in detergent compositions by subjecting these mixtures to sulfonation, neutralization and drying, as indicated hereinbefore with respect to blending with individual 2-phenyl alkanes.

The 2-phenyl alkanes, from which corresponding water-soluble organic sulfonates, suitable as anti-caking additives in accordance with the invention, may be readily derived, can be prepared by any appropriate method, e.g., by condensation (alkylation) of benzene with normal 1-olefins containing from 10 to 16 carbon atoms. Mild alkylation conditions are preferably employed to insure the formation of a predominance of 2-phenyl alkane in the alkylation product.

To compare the anti-caking effect of these 2-phenyl alkane sulfonate salts in the detergent compositions with the extent of caking in conventional compositions containing but 40% by weight of a water-soluble organic salt of sulfonated monophenyl - substituted acyclic C_9 to C_{18} propylene polymers (the remainder being inorganic sulfate), the following procedure was adapted in the laboratory:

Acetophenone was reacted with a Grignard reagent, e.g. normal 1-decyl magnesium bromide. The resulting product was hydrolyzed to form an alcohol which was then dehydrated to yield 2-phenyl dodecene, and this latter was hydrogenated. After fractionally distilling the hydrogenation product at reduced pressure in a spinning band column and passing the distillate through silica gel to insure the presence of substantially pure 2-phenyl dodecane, this latter product was sulfonated by adding 2.6 moles of 20% oleum per each mole of hydrocarbon at 90° F., and digesting at 113° F. for 5 hours. The resulting mixture of sulfonated 2-phenyl dodecane and unreacted sulfuric acid was subsequently neutralized with a 20% aqueous solution of sodium hydroxide to a pH of 7.0. If necessary, sodium sulfate was then added to the final neutralized sulfonate-sulfate slurry in order to adjust its content of solids to 40% of sodium 2-phenyl dodecane sulfonate and 60% of sodium sulfate, whereupon the slurry was drum-dried and comminuted to the dried flake or chip form.

The ultimate particulate sodium salt of sulfonated 2-phenyl dodecane, prepared as described hereinbefore, dissolved in water at 113° F. to the extent of 22.4% by weight. The surface tension of the aqueous solutions of this product ranged from 37.7 to 52.3 dynes/cm. at 70° F., depending on the concentration which ranged correspondingly from 0.25% to 0.005%. Its detergency at 0.4% concentration in hard water (300 ppm) measured by the Launderometer Method (see Ind. Eng. Chem., Vol. 41, Feb. 1949, pp. 423) was found not only to be equal, but, in fact, slightly better than that of a solution of an equal concentration of 40% sodium sulfonated monophenyl-substituted C_{12} to C_{15} propylene polymers and 60% sodium sulfate.

A number of test runs have been made to compare the extent of caking in compositions in which the effective organic detergent ingredient was a water-soluble organic salt of sulfonated monophenyl-substituted propylene polymers containing from 9 to 18 carbon atoms, and in compositions prepared in accordance with the present invention, in which the effective organic detergent ingredient consisted essentially of a mixture of a water-soluble salt composed of an inorganic cation and sulfonated monophenyl-substituted C_9—C_{18} propylene polymers with at least 20% by weight of a water-soluble salt composed of an identical cation and a sulfonated 2-phenyl alkane wherein the alkane portion was a normal alkane having from 10 to 16 carbon atoms. Furthermore, the caking tendency of corresponding water-soluble salts composed of inorganic cations and sulfonated 2-phenyl alkanes as such has also been observed.

The extent of caking was determined in accordance with the following procedure: Weighed samples of dry solid particulate detergent compositions were placed in small untreated sealed cardboard boxes ($1\frac{1}{2}'' \times 2\frac{1}{2}'' \times 4''$). Three samples of each detergent composition were used in each test. These samples were placed into a humidity cabinet in a completely random manner and exposed to a relative humidity of about 80% at a temperature of about 90° F. for a period of one week. At the end of this exposure period, all samples were re-weighed, and the extent of caking was determined by first cutting away an entire side of each cardboard box, and then carefully transferring the sample onto a No. 4 sieve ($\frac{1}{4}''$ mesh) from a minimum height. The sieve was then gently swirled until all particles

came into contact with the screen. Material which did not pass through the screen in this treatment was considered to be caked. The results of these test runs unambiguously indicated a remarkable reduction of caking, owing to the blending of water-soluble salts composed of inorganic cations and sulfonated monophenyl-substituted C_9—C_{18} propylene polymers with salts composed of like inorganic cations and sulfonated 2-phenyl C_{10}—C_{16} alkanes.

The following Table contains data from a representative series of 7 test runs in which the first 3 runs, Nos. 1, 2 and 3, were made on a detergent composition containing sodium salt of sulfonated monophenyl-substituted propylene polymers having from 12 to 15 carbon atoms in the polymer chain (40% active sulfonate detergent, remainder sodium sulfate builder), and blended with sodium 2-phenyl dodecane sulfonate (also containing 40% sulfonate, remainder being sodium sulfate), in acordance with the invention. The relative amounts of sodium 2-phenyl dodecane sulfonate additive varied from 20 to 60% of the total weight of organic sulfonate detergent ingredients of the blend. Run 4 was carried out, employing only sodium 2-phenyl dodecane sulfonate used for blending in Runs 1, 2 and 3. Run 5 was carried out by employing untreated detergent compositions containing sodium salt of monophenyl-substituted C_{12}—C_{15} propylene polymers (40% active sulfonate, remainder Na_2SO_4), without blending with sodium 2-phenyl dodecane sulfonate. Runs 6 and 7 were effected by employing sodium 2-phenyl decane and tetradecane sulfonates, respectively, prepared similarly to sodium 2-phenyl dodecane sulfonate of Run 4.

TABLE

COMPARISON OF CAKING IN DETERGENT COMPOSITIONS

Test Conditions: Relative humidity = 80%; temperature = 90° F.
Duration of test = 7 days.
All samples contained 40% of active detergent sulfonates and 60% Na_2SO_4

Run No.	1	2	3	4	5	6	7
Sodium monophenyl-substituted C_{12}—C_{15} propylene polymer sulfonates, % by wt.	80	60	40	—	100	—	—
Sodium 2-phenyl decane sulfonate, % by wt.	—	—	—	—	—	100	—
Sodium 2-phenyl dodecane sulfonate, % by wt.	20	40	60	100	—	—	—
Sodium 2-phenyl tetradecane sulfonate, % by wt.	—	—	—	—	—	—	100
% caked, based on the weight of the whole composition in a cardboard container	7.0	2.0	3.0	1.0	79.00	2.3	0.9

The results of this representative series of tests in the Table clearly show the remarkable reduction of the caking tendency in detergent compositions, containing water-soluble salts composed of inorganic cations and sulfonated monophenyl-substituted propylene polymers with 9 to 18 carbon atoms in the polymer portion, by the introduction of from at least 20% to about 95% by weight of a corresponding water-soluble sulfonate salt composed of the same inorganic cation and 2-phenyl alkanes containing from 10 to 16 carbon atoms in their alkane portion.

What we claim is:—

1. A detergent composition characterized by resistance to caking and containing as active organic detergent components a water-soluble salt composed of an inorganic cation and a mixture of sulfonated monophenyl - substituted acyclic propylene polymers having from

9 to 18 carbon atoms in the polymer chain, and at least 20% by weight based on the total weight of the sulphonates of a water-soluble salt composed of the same inorganic cation and a sulfonated 2-phenyl alkane in which the alkane portion is a straight-chain normal alkane containing from 10 to 16 carbon atoms.

2. A detergent composition as claimed in claim 1, in which said propylene polymers contain from 12 to 15 carbon atoms in the polymer chain.

3. A detergent composition as claimed in claim 1 or 2, in which said water-soluble salts are sodium salts.

4. A detergent composition as claimed in any preceding claim, wherein said alkane portion of sulfonated 2-phenyl alkane is a normal dodecane.

5. A built detergent composition containing from 40 to 85% by weight of inorganic builders and 15 to 60% by weight of a detergent composition as claimed in any of the preceding claims.

6. A built detergent composition substantially as hereinbefore described.

HASELTINE, LAKE & CO.,
28, Southampton Buildings,
London, W.C.2, and
19—25, West 44th Street,
New York, U.S.A.
Agents for the Applicants.

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